Supplementary Information

S1 Estimation of the air exchange rate in the laboratory

During a period of constant NO_3 reactivity, a bottle of pure *S*-(-)-limonene (96%, Sigma-Aldrich) was opened in the center of the room for 15 s at 12:37 UTC. The resulting signal in the NO_3 reactivity setup is depicted in Fig. S1a. At 12:38 UTC, i.e. within approx. 1 min after release of limonene, the initial NO_3 mixing ratio $[NO_3]_0$ of 54 pptv (resulting from the instrument's source) is depleted to ca. 35 pptv when sampling the ambient air. It took ca. 20 min for the signal to recover. In order to estimate the exchange rate, $[NO_3]_0$ was subtracted from the signal and plotted against the time after the release of limonene. An exponential decay fit (Fig. S1b) indicates an exchange rate of 0.0016 s^{-1}, which corresponds to 5.76 h^{-1}. This exchange rate is comparable to those found in common ventilated commercial or office buildings that typically feature mechanically-assisted exchange rates between 0.5 and 9 h^{-1}.[1, 2] However, these values clearly exceed the mean exchange rate for residential buildings of 0.5 h^{-1}, but even in domestic indoor environments exchange rates of 2.3 h^{-1} have been reported.[3] The conditions found in our laboratory are thus more representative for non-domestic indoor environments.

Our value was derived under the assumption, that the ventilation is the only loss process of limonene whereas limonene may be oxidized by OH, O_3 and NO_3. Using indoor mixing ratios of 18 ppbv O_3 (measured during the experiment) and 1 pptv NO_3, assuming an indoor OH mixing ratio of 10^5 molecules cm^{-3} [4, 5] and applying the corresponding rate coefficients for their reaction with limonene[6] yields a loss rate of ~ 4×10^{-4} s^{-1}. Under these assumptions, gas-phase reactions would bias the exchange rate high by 27%. In addition to the gas-phase losses, heterogeneous processes, e.g. deposition on surfaces or particles would bias the estimated $k_{exchange}$ to higher values. For these reasons, the experiment was repeated with 2,3-dimethyl-2-butene (DMB, 98%, Sigma-Aldrich) as tracer gas. This compound has similar rate coefficients for reactions with NO_3 and OH and its rate coefficient towards O_3 is one order of magnitude higher. At the same time, the vapor pressure of DMB (~ 128 Torr at 298 K[7]) is much higher than that of limonene (~ 1.6 Torr at 298 K[8]) which should lead to reduced deposition loss rates on surfaces. An analogous experiment carried out with DMB is depicted in Fig. S1c and yields a very similar exchange rate of 0.0012 s^{-1} (4.3 h^{-1}).

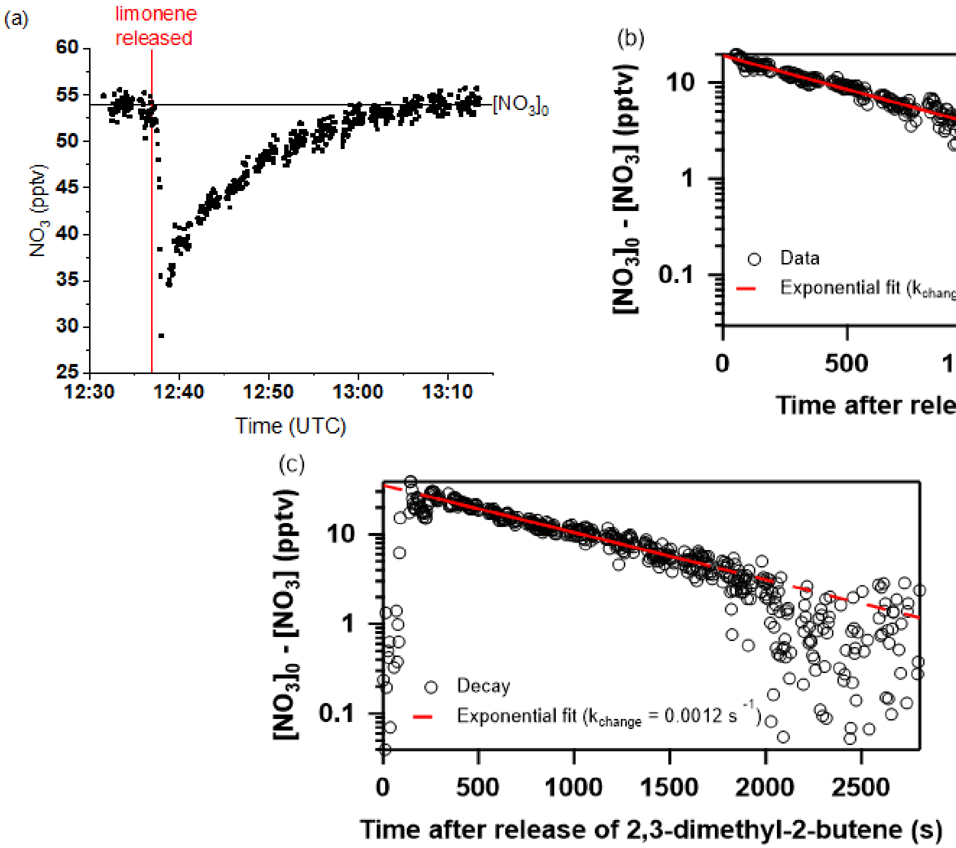

Figure S1. Estimation of the air exchange rate using the tracer-gas approach with limonene (or 2,3- dimethyl-2-butene, DMB). The tracer gas was measured indirectly by monitoring the NO_3 reactivity: (a) Time-series of observed NO_3 mixing from the source while sampling diluted ambient air during the experiment with limonene. Difference between initial and measured NO_3 mixing ratios (logarithmic scale) with time after release of (b) limonene and (c) DMB. In both cases, the red line shows the regression of the data (solid part marks fitting interval) with an exponential decay function ($y = A \times \exp[-k_{change} \times t]$).

S2 Indoor photolysis rate constants of NO_2 and NO_3

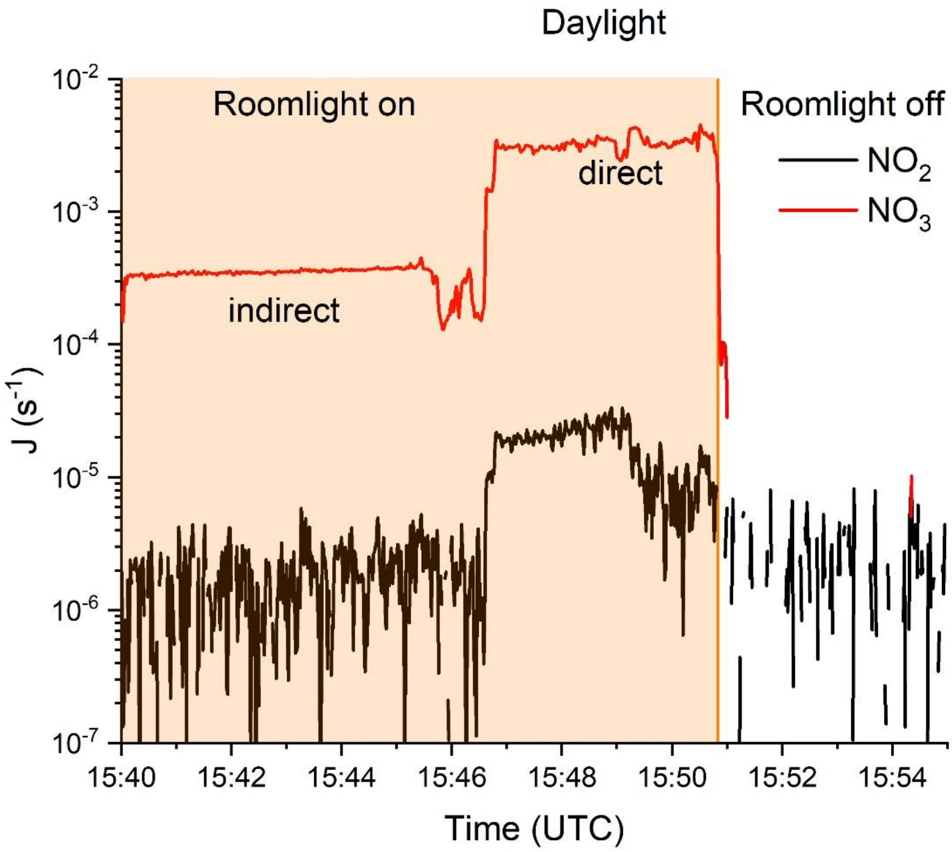

Figure S2: Photolysis rates of NO_2 (black) and NO_3 (red) inside the laboratory with room light switched on (orange-shaded area) and off. When the room-light was turned off, the photolysis rates of both species are below the LOD of 10^{-6} s^{-1}.

S3 NO_2 measurement intercomparison

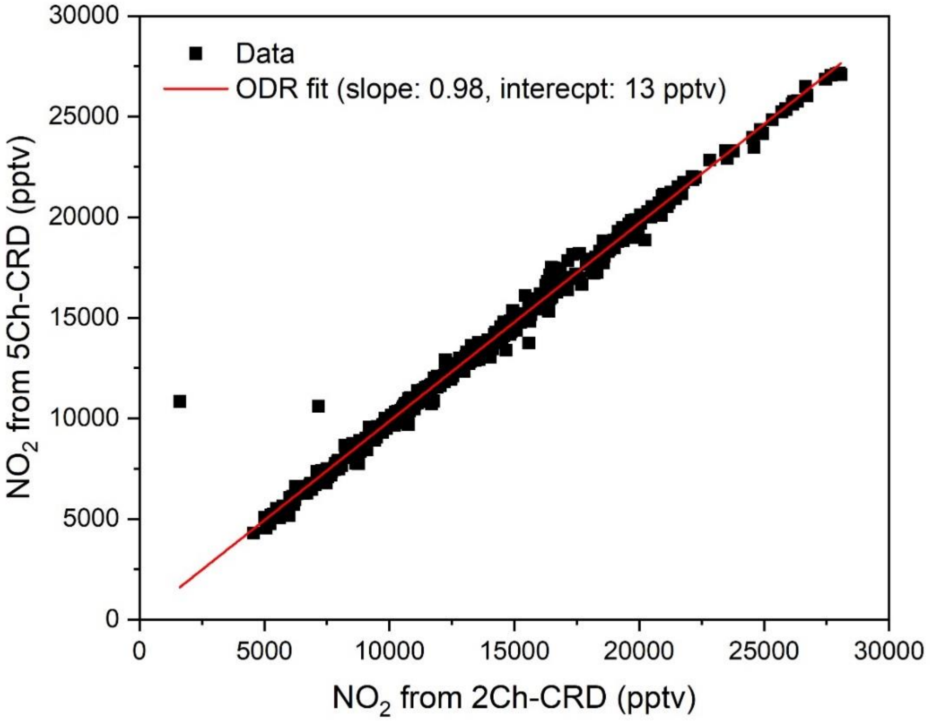

Figure S3: Plot of NO_2 mixing ratios measured with the 5Ch-CRD spectrometer and the 2Ch-CRD spectrometer. An orthogonal distance regression (red line, ODR fit, Pearson correlation coefficient r = 0.99) yields a slope of 0.98 and an intercept of 13 pptv.

S4 Contamination of inlet filter for NO_3/N_2O_5 measurements

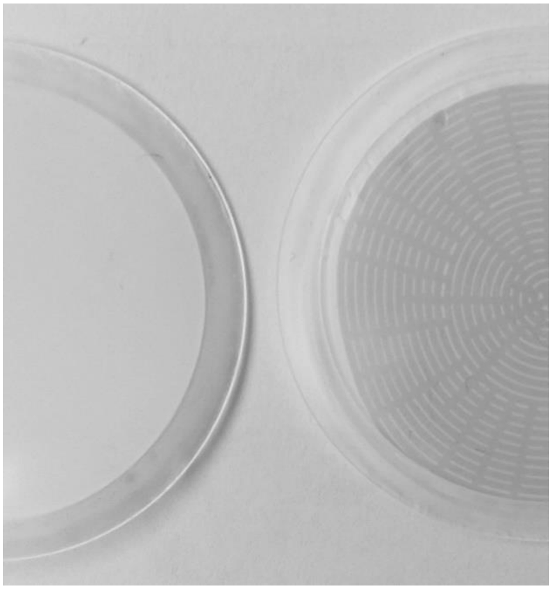

Figure S4: Comparison between a fresh inlet filter (left) and the one used during the measurements of NO_3 and N_2O_5 inside the laboratory (right).

References

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